

TRANSLATION

(12) PRELIMINARY PUBLISHED APPLICATION

(18) FEDERAL REPUBLIC
OF GERMANY

(10) DE 196 27 071 A 1

(51) Int. Cl.⁶:
H 05 B 33/02
C 09 K 11/06
C 08 G 61/12

GERMAN
PATENT OFFICE

(21) File number: 196 27 071.5
(22) Date of Application: 07/05/96
(43) Date of disclosure: 01/08/98

(71) Applicant:

Bayer AG, 51373 Leverkusen, DE

(72) Inventor:

Jonas, Friedrich, Dr., 52066 Aachen, DE; Eischner,
Andreas, Dr., 45479 Munich, DE; Wehrmann, Rolf, Dr.,
47800 Krefeld, DE; Quintens, Dirk, Dr., Lier, BE

(54) Electroluminescent arrangement

(57) Electroluminescent arrangements,
which contain hole- and/or electron-
injecting layers, whereby the polymeric
organic conductors are selected from the
group of polyfurans, polypyrrols,
polyanilines, polythiophenes and
polypyridines.

Description

The invention concerns electroluminescent arrangements, which contain conductive polymers as a hole- and/or electron-injecting layer.

An electroluminescent (EL) arrangement is characterized in that it emits light by applying an electric voltage under current conduction. Such arrangements have been known for a long time in technology under the designation "light emitting diodes" (LEDs). The emission of light occurs in that positive charges (holes) and negative charges (electrons) combine whereby light is emitted.

The LEDs commonly used in technology predominantly consist of inorganic semiconductor materials. However, EL-arrangements have been known for several years, the main components of which are organic materials.

These organic EL-arrangements generally contain one or several layers consisting of organic charge transport compounds.

The principal layer construction is as follows. The numbers 1 to 10 thereby represent:

- 1 carrier, substrate
- 2 base electrode
- 3 hole-injecting layer
- 4 hole-transporting layer
- 5 emitter-layer
- 6 electron-transporting layer
- 7 electron-injecting layer
- 8 top electrode
- 9 contacts
- 10 jacketing, encapsulation

This construction represents the general case and can be simplified, in that individual layers are omitted, so that one layer assumes several tasks. In the simplest

case, an EL-arrangement consists of two electrodes, between which an organic layer is located, which fulfills all functions – including that of the emission of light. Such systems are described, for examples in the Application WO 9013148 based on poly-[p-phenylenevinylene].

When producing large-surface, electroluminescent display elements, at least one of the current-supplying electrodes 2 or 8 must consist of a transparent and conductive material.

Transparent carriers such as glass or plastic films (for example polyester, such as polyethylene terephthalate or polyethylene naphthalate, polycarbonate, polyacrylate, polysulphone, poly-imide-film) are suitable as substrate 1.

The following are suitable as transparent and conductive materials:

- a) metallic oxides, for example indium-tin-oxide (ITO), tin oxide (NESA), etc.
- b) semi-transparent metallic films, for example Au, Pt, Ag, Cu etc.

Suitable as emitter layer 5 are, for example:

In the applications according to the invention, low molecular weight materials or oligomers as well as also polymeric materials can be used as emitter layer 5. The substances distinguish themselves in that they are photoluminescent. That means that fluorescent dyes and/or fluorescent molecules and their conversion products to oligomers or their incorporation into polymers are suitable.

Examples for such materials are cumarins, perylenes, anthracenes, phenanthrenes, stilbenes, distyryls, methines or metal complexes, such as Alq_3 etc. Suitable as polymers are possibly substituted phenylenes, phenylene vinylene or polymers with fluorescent segments in the polymer side chain or in the polymer backbone. A comprehensive summary is given in EP-A 532 798.

However, it became obvious in the practical application that electron- and/or hole-injecting layers (3, 4 and/or 6, 7) must be incorporated into the electroluminescent structures in order to increase the radiant intensity per unit area.

A large number of organic compounds, which transport charges (holes and/or electrons) is described in the literature. Predominantly low molecular weight substances

are used, which are, for example, subjected to a high vacuum metallization. For example, the publications EP-A 387 715, US-A 4 539 507, 4 720 432 and 4 769 292 provide a good survey regarding the substance classes and their use.

A disadvantage hereby is the application by high vacuum metallization. In order to simplify the production process of ELP displays it would be advantageous if the layers 3, 4 and 6, 7 can be produced, for example, by application from solution.

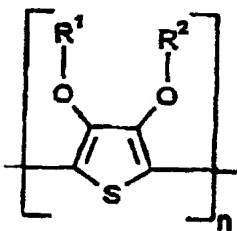
It is known from EP-A 686 662 to employ special mixtures consisting of conductive organic polymeric conductors, such as 3,4-polyethylenedioxythiophene and polyhydroxy compounds or lactams as electrode 1 in ELP-structures.

In Synthetic Metals (1996) 141 – 143, poly-(3,4-ethylenedioxythiophene) is also described as an electrode in LED's, whereby it is pointed out that poly-(3,4-ethylenedioxythiophene) leads to lower luminances compared to indium tin oxide (ITO).

It was now surprisingly found that pure polymeric organic conductors such as 3,4-polyethylenedioxythiophene as charge-initiating intermediary layer on transparent metal electrodes such as ITO afford luminances in LED's, which are clearly superior to the LED's with pure metal electrodes and/or pure conductive polymer electrodes. These layers can be produced from solution or by direct polymerization of the monomers corresponding to the polymeric organic conductors.

Suitable organic conductors are, for example, polyfurans, polypyrrols, polyanilines or polythiophenes, polypyridines. These are described, for example, in EP-A 257 573 (polyalcoxythiophene), WO 90/04256 (polyaniline), EP-A 589 529 (polystyrene), DE-A 22 62 743 (oligoanailines).

Particularly suitable are neutral or cationic thiophenes of the formula (I)



(I),

whereby,

R^1 and R^2 represent, independently from one another, hydrogen, if applicable substituted C_1 – C_{20} -alkyl, CH_2OH or C_6 – C_{14} -aryl or

R^1 and R^2 together represent $-(CH_2)_m - CH_2$ with $m = 0$ to 12 , preferably 1 to 5 , C_6 – C_{14} -arylene and n stands for a whole number from 5 to 100 .

R^1 and R^2 preferably represent $-(CH_2)_l - CH_2$ with $l = 1$ to 4 .

The polythiophenes of the recurring structure unit of formula I) are known (compare EP-A 440 958 and 339 340). The production of the dispersions and/or solutions, according to the invention, is described in EP-A 440 957 and DE-OS 42 11 459.

Polythiophenes are preferably used in the dispersion and/or solutions in cationic form as they are obtained, for example, by treating the neutral thiophenes with oxidation agents. Standard oxidation agents, such a potassium peroxodisulfate, are used for the oxidation. As a result of the oxidation, the polythiophenes receive positive charges, which are not shown in the formulas, since their number and their position cannot be clearly determined. According to data in EP-A 339 340, they can be produced directly on carriers.

The subjects of the invention are therefore electroluminescent arrangements, which contain hole- and/or electron-injecting layers consisting of the above mentioned polymeric organic compounds.

Subject of this invention is furthermore the use of the stated polymeric organic compounds as hole- and/or electron-injecting substances.

For example, with the system according to the invention, a solution of 3,4-polyethylenedioxythiophene is distributed on the base electrode in the form of a film. As solvent one preferably uses water and/or water alcohol mixtures. Suitable alcohols are, for example, methanol, ethanol, propanol, isopropanol.

The use of these solvents has the advantage that other layers of organic solvents, such as aromatic or aliphatic hydrocarbon mixtures, can then be applied without attacking the layer 3, 4. The same is true for the application of layer 6, 7 onto the emitter layer 5.

The solution of the polymeric organic conductor is evenly distributed upon the substrate by techniques such as spin coating, casting, doctoring, printing, etc. The layers

are subsequently dried at room temperature or temperatures up to 300°C, preferably 200°C.

The thickness of the intermediary layer is approximately 3 to 100 nm, typically it is 10 nm.

Organic, polymeric binding agents and/or organic, low molecular weight cross-linking agents can be added additionally to the solutions of the polymeric organic conductors. Suitable binding agents are, for example, described in EP-A 564 911.

The intermediary layers 3, 4, according to the invention, can also be produced on the base electrode by electrochemical polymerization of the monomers analogous to the polymeric organic conductors. These processes are known and are described, for example, in EP 339 340.

Examples

The production of 3,4-polyethylenedioxythiophene (PEDT/PSS parent solution)

20 g of free polystyrene sulphonic acid (Mn approximately 40 000), 21.4 g of potassium peroxodisulfate and 50 mg of iron(III)-sulfate are introduced into 2000 ml water with stirring. While stirring, 8.0 g of as 3,4- ethylenedioxythiophene are added. The solution is stirred for 24 hours at room temperature. Then 100 g of anion exchanger (commercial product Bayer AG Lewatit MP 62) and 100 g of cation exchanger (commercial product Bayer AG Lewatit S 100), both water damp, are added and the mixture is stirred for 8 hours.

The ion exchangers are removed by filtration. A solution with a solid material content of approximately 1.2 weight-% is obtained, which is ready-to-use.

Example 1

When producing an electroluminescent arrangement with PEDT/PSS-intermediary layer, according to the invention, the following procedure was employed.

a) Purification of ITO

Glass coated with ITO (produced by Balzers) is cut into 20 x 30 mm pieces and purified by the following steps:

1. 15 minutes in distilled water/Falterol-rinsing agent (basic) ultrasonic bath rinsing 2 times for 15 minutes in freshly distilled water each in the ultrasonic bath,
2. 15 minutes in ethanol in the ultrasonic bath,
3. 2 times for 15 minutes in fresh acetone each in the ultrasonic bath,
4. Drying on lint-free lens cloths.

b) Application of the PEDT/PSS-layer onto the ITO

2 Volume-parts of the filtered PEDT/PSS-parent solution are mixed with 1 volume portion of methanol. Approximately 1 ml of this solution is distributed on the purified ITO-substrate. The excess solution is centrifuged off with a spin coater for 30 seconds at 1500 revolutions per minute. The film is subsequently dried in the drying chamber for 20 minutes at 70°C. The layer thickness is determined with a stylusprofilometer (Tencor 200) to be 50 nm.

c) Application of the electroluminescent layer

A second layer, the electroluminescent layer, is applied onto the dried PEDT/PSS-layer. For this, a 1-% solution consisting of 7 parts per weight poly(vinylcarbazol) (PVK) (Aldrich) and 3 parts per weight of methine dye (EP-A 699 730) is produced. The solution is filtered and 1 ml of the solution is distributed on the PEDT/PSS. The excess solution is centrifuged off with a spin-coater for 30 seconds at 1000 revolutions per minute. Then the sample is dried in the vacuum oven for 20 minutes at 50°C. The total layer thickness of the sample is then 150 mn.

d) Vacuum metallizing of the metal-electrodes and electrical bonding

The sample is built into a vacuum metallization apparatus (Leybold 600). A hole-mask with a hole diameter of 3 mm is placed onto the polymer layer. At a pressure of 10^{-5} mbar, Al is vaporized from a target with the help of an electron-beam canon towards the polymer layer. The Al-layer has a thickness of 500 nm. The two electrodes of the organic LED are connected with the power source via electric feeders. The positive pole is connected with the ITO-electrode, the negative pole with the Al-electrode.

e) Determination of the electroluminescence

A current of $1\text{mA}/\text{cm}^2$ already flows through the arrangement at small voltages ($U = 5$ volt). At 8 volts, electroluminescence can be detected with a photodiode. At 20 volts, the electroluminescence intensity is $50\text{ cd}/\text{m}^2$ (Minolta, LS 100).

The control experiment without the PEDT/PSS-intermediary layer, according to the invention, leads to lower EL-intensities and to higher cutoff voltage.

Example 2

The following procedure was used during the production of an electroluminescent arrangement with PEDT/PSS-intermediary layer, according to the invention.

a) Purification of the ITO

Glass coated with ITO (produced by Balzers) is cut into 20 x 30 mm pieces and purified by the following steps:

1. 15 minutes in distilled water/Falterol-rinsing agent (basic) ultrasonic bath
2. rinsing 2 times for 15 minutes in freshly distilled water each in the ultrasonic bath,
3. 15 minutes in ethanol in the ultrasonic bath,
4. 2 times for 15 minutes in fresh acetone each in the ultrasonic bath,

5. Drying on lint-free lens cloths.

b) Application of the PEDT/PSS-layer onto ITO

2 Volume-parts of the filtered PEDT/PSS-parent solution are mixed with 1 volume part methanol. Approximately 1 ml of this solution is distributed on the purified ITO-substrate. The excess solution is centrifuged off with a spin coater for 30 seconds at 1500 revolutions per minute. The film is subsequently dried in the drying chamber for 20 minutes at 70°C. The layer thickness is determined by a stylusprofilometer (Tencor 200) to be 50 nm.

c) Application of the electroluminescent layer

A second layer, the electroluminescent layer, is applied onto the dried PEDT/PSS-layer. For this, a 1.5-% solution consisting of 7 parts per weight poly(vinylcarbazol) (PVK) (Aldrich) and 3 parts per weight of cumarine 6 (Lambda Physics) is produced. The solution is filtered and 1 ml of the solution is distributed onto the PEDT/PSS. The excess solution is centrifuged off with a spin-coater for 10 seconds at 1800 revolutions per minute.

d) Vacuum metallizing of the metal-electrodes and electrical bonding

The sample is built into a vacuum metallization apparatus (Leybold 600). A hole-mask with a hole diameter of 3 mm is placed onto the polymer layer. At a pressure of 10^{-5} mbar, Al is vaporized from a target with the help of an electron-beam canon towards the polymer layer. The Al-layer has a thickness of 500 nm. The two electrodes of the organic LED are connected with the power source via electric feeders. The positive pole is connected with the ITO-electrode, the negative pole with the Al-electrode.

e) Determination of the electroluminescence

A current of $1\text{mA}/\text{cm}^2$ already flows through the arrangement at small voltages ($U = 10$ volts). At 8 volts, electroluminescence can be detected with a photodiode. At 20 volts, the electroluminescence intensity is $10\text{ cd}/\text{m}^2$ (Minolta, LS 100).

Example 3

When producing an electroluminescent arrangement with PEDT/PSS-intermediary layer, according to the invention, the following procedure was employed.

a) Purification of ITO

Glass coated with ITO (produced by Balzers) is cut into 20×30 mm pieces and purified by the following steps:

1. 15 minutes in distilled water/Falterol-rinsing agent (basic) ultrasonic bath,
2. rinsing 2 times for 15 minutes in freshly distilled water each in the ultrasonic bath,
3. 15 minutes in ethanol in the ultrasonic bath,
4. 2 times for 15 minutes in fresh acetone each in the ultrasonic bath,
5. Drying on lint-free lens cloths.

b) Application of the PEDT/PSS-layer onto the ITO

2 Volume-parts of the filtered PEDT/PSS-parent solution are mixed with 1 volume part methanol. Approximately 1 ml of this solution is distributed on the purified ITO-substrate. The excess solution is centrifuged off with a spin coater for 30 seconds at 1500 revolutions per minute. The film is subsequently dried in the drying chamber for 20 minutes at 70°C . The layer thickness is determined with a stylusprofilometer (Tencor 200) to be 50 nm.

c) Application of the electroluminescent layer

A second layer, the electroluminescent layer, is applied onto the dried PEDT/PSS-layer. For this, a 1.5-% solution consisting of 7 parts per weight poly(vinylcarbazol) (PVK) (Aldrich) and 3 parts per weight of perylene dye KF 856 (commercial product of BASF) is produced. The solution is filtered and 1 ml of the solution is distributed onto the PEDT/PSS. The excess solution is centrifuged off with a spin-coater for 10 seconds at 1800 revolutions per minute. The total layer thickness of the sample is then 140 nm.

d) Vacuum metallizing of the metal-electrodes and electrical bonding

The sample is built into a vacuum metallization apparatus (Leybold 600). A hole-mask with a hole diameter of 3 mm is placed onto the polymer layer. At a pressure of 10^{-5} mbar, Al is vaporized from a target with the help of an electron-beam canon towards the polymer layer. The Al-layer has a thickness of 500 nm. The two electrodes of the organic LED are connected with the power source via electric feeders. The positive pole is connected with the ITO-electrode, the negative pole with the Al-electrode.

e) Determination of the electroluminescence

A current of 1 mA/cm^2 already flows through the arrangement at small voltages ($U = 5 \text{ volt}$). At 4 volts, electroluminescence can be detected with a photodiode. At 15 volts, the electroluminescence intensity is 30 cd/m^2 (Minolta, LS 100).

The control experiment without the PEDT/PSS-intermediary layer, according to the invention, leads to lower EL-intensities and to higher cutoff voltage.

Example 4

- a) An ITO-substrate, purified according to example 1a and a platinum foil ($1 \times 2 \text{ cm}^2$) is suspended into a solution consisting of 0.8 g of tetramethyl ammonium tetrafluoroborate and 0.28 g of 3,4 ethylene dioxythiophene in 100 ml acetonitrile. The glass plate is wired as the anode. At a voltage of 2 V and a current of 1.5 mA, a thin 3,4-polyethylenedioxythiophene layer separates in 20 seconds as the hole-injecting intermediary layer.
- b) A second layer, the electroluminescent layer, is applied onto the dried PEDT-layer. A 1-% solution consisting of 7 parts per weight poly(vinylcarbazol) (PVK) (Aldrich) and 3 parts per weight of methine dye (EP-A 699 730) is produced for this. The solution is filtered and 1 ml of the solution is distributed onto the PEDT. The excess solution is centrifuged off with a spin-coater for 30 seconds at 1000 revolutions per minute. The sample is subsequently dried in the vacuum oven for 20 minutes at 50°
- c) Vacuum metallizing of the metal-electrodes and electrical bonding

The sample is built in a vacuum metallization apparatus (Leybold 600). A hole-mask with a hole diameter of 3 mm is placed onto the polymer layer. At a pressure of 10^{-5} mbar, Al is vaporized from a target with the help of an electron-beam canon towards the polymer layer. The Al-layer has a thickness of 500 nm. The two electrodes of the organic LED are connected with the power source via electric feeders. The positive pole is connected with the ITO-electrode, the negative pole with the Al-electrode.

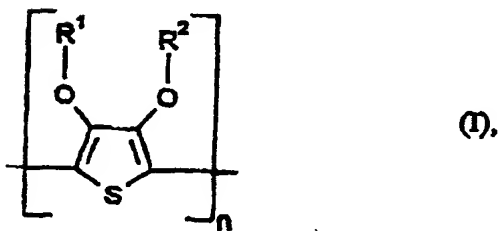
- e) Determination of the electroluminescence

A current of 1 mA/cm^2 already flows through the arrangement at small voltages ($U = 5 \text{ volt}$). At 4 volts, electroluminescence can be detected with a photodiode. At 20 volts, the electroluminescence intensity is 10 cd/m^2 (Minolta, LS 100).

The control experiment without the PEDT/PSS-intermediary layer, according to the invention, leads to lower EL-intensities and to higher cutoff voltage.

Patent Claims

1. Electroluminescent arrangements, which contain hole- and/or electron-injecting layers, whereby the polymeric organic conductors are selected from the group of polyfurans, polypyrrols, polyanilines, polythiophenes and polypyridines.
2. Electroluminescent arrangement according to claim 1, whereby neutral or cationic thiophenes of formula (I)



are used, whereby

R¹ and R², independent from one another, represent hydrogen, if applicable, substituted C₁– C₂₀-alkyl, CH₂OH or C₆– C₁₄-aryl or

R¹ and R² together represent –(CH₂)_m – CH₂ with m = 0 to 12, preferably 1 to 5, C₆– C₁₄-arylene and

n stands for a whole number from 5 to 100.

3. The use of polymeric organic compounds according to claims 1 and 2 as conductor in hole- and/or electron-injecting layers of electroluminescent arrangements.

James E. Alexander

March 18, 2002